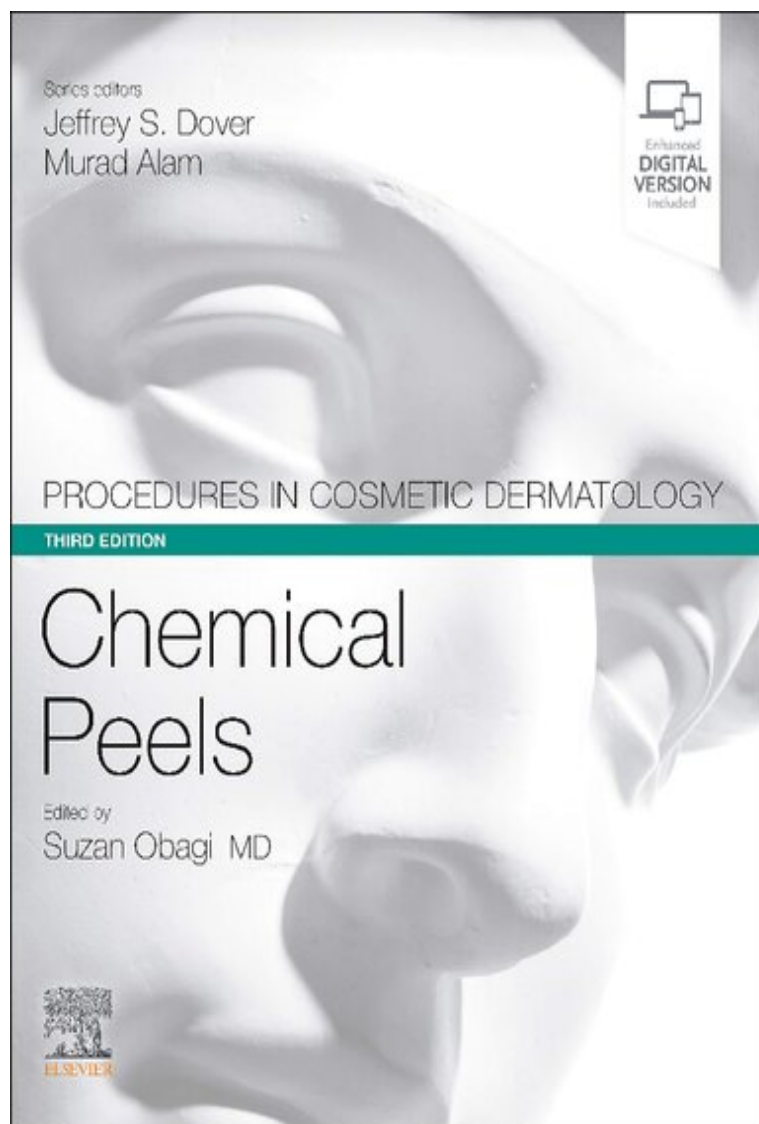


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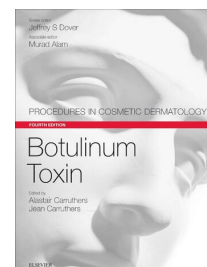


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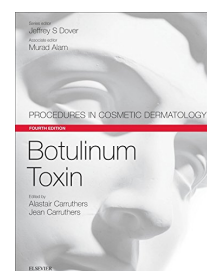
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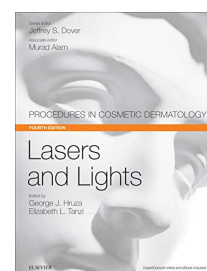
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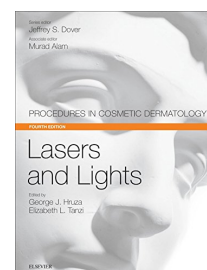
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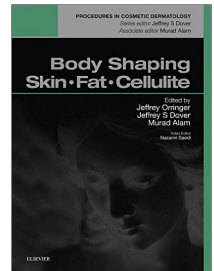
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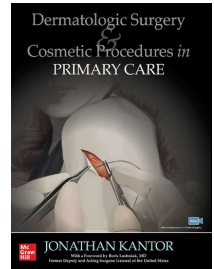
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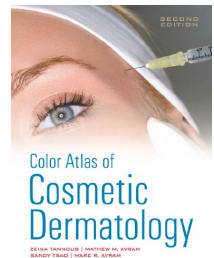
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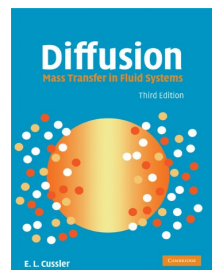
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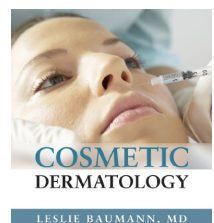
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Chemical Peels

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SERIES PREFACE, FIRST EDITION

While dermatologists have been procedurally inclined since the beginning of the specialty, particularly rapid change has occurred in the past quarter century. The advent of frozen section technique and the golden age of Mohs skin cancer surgery has led to the formal incorporation of surgery within the dermatology curriculum. More recently, technological breakthroughs in minimally invasive procedural dermatology have offered an aging population new options for improving the appearance of damaged skin.

Procedures for rejuvenating the skin and adjacent regions are actively sought by our patients. Significantly, dermatologists have pioneered devices, technologies, and medications that have continued to evolve at a startling pace. Numerous major advances, including virtually all cutaneous lasers and light-source based procedures, botulinum exotoxin, soft tissue augmentation, dilute anesthesia liposuction, leg vein treatments, chemical peels, and hair transplants, have been invented or developed and enhanced by dermatologists. Dermatologists understand procedures, and we have special insight into the structure, function, and workings of skin. Cosmetic dermatologists have made rejuvenation accessible to risk-averse patients by emphasizing safety and reducing operative trauma. No specialty is better positioned than dermatology to lead the field of cutaneous surgery while meeting patient needs.

As dermatology grows as a specialty, an ever-increasing proportion of dermatologists will become proficient in the delivery of different procedures. Not all dermatologists will perform all procedures, and some will perform very few, but even the less procedurally directed among us must be well-versed in the details to be able to guide and educate our patients. Whether you are a skilled dermatologic surgeon interested in further expanding your surgical repertoire, a complete surgical novice wishing to learn a few simple procedures, or somewhere in between, this book and this series are for you.

The volume you are holding is one of a series entitled *Procedures in Cosmetic Dermatology*. The purpose of each book is to serve as a practical primer on a major topic area in procedural dermatology.

If you want to make sure you find the right book for your needs, you may wish to know what this book is and

what it is not. It is not a comprehensive text grounded in theoretical underpinnings. It is not exhaustively referenced. It is not designed to be a completely unbiased review of the world's literature on the subject. At the same time, it is not an overview of cosmetic procedures that describes these in generalities without providing enough specific information to actually permit someone to perform the procedures. And importantly, it is not so heavy that it can serve as a doorstop or shelf filler.

What this book and this series offer is a step-by-step, practical guide to performing cutaneous surgical procedures. Each volume in the series has been edited by a known authority in that subfield. Each editor has recruited other equally practical-minded, technically skilled, hands-on clinicians to write the constituent chapters. Most chapters have two authors to ensure that different approaches and a broad range of opinions are incorporated. On the other hand, the two authors and the editors also collectively provide a consistency of tone. A uniform template has been used within each chapter so that the reader will be easily able to navigate all the books in the series. Within every chapter the authors succinctly tell it like they do it. The emphasis is on therapeutic technique; treatment methods are discussed with an eye to appropriate indications, adverse events, and unusual cases. Finally, this book is short and can be read in its entirety on a long plane ride. We believe that brevity paradoxically results in greater information transfer because cover-to-cover mastery is practicable.

Most of the books in the series are accompanied by videos that demonstrate the procedures discussed in that text. Some of you will turn immediately to the video and use the text as a backup to clarify complex points, whereas others will prefer to read first and then view the video to see the steps in action. Choose what suits you best.

We hope you enjoy this book and the rest of the books in the series and that you benefit from the many hours of clinical wisdom that have been distilled to produce it. Please keep it nearby where you can reach for it when you need it.

**Jeffrey S. Dover, MD, FRCPC,
Murad Alam, MD, MSCI**

SERIES PREFACE, THIRD EDITION

As this *Procedures in Cosmetic Dermatology* series undergoes another iteration, it is clear our mission that was initiated 15 years ago to provide succinct and current expert guidance regarding particular cosmetic procedures remains highly relevant. Our portable, travel-ready format continues to match the ever-shortening attention span of the overwhelmed physician. Indeed, similar series of slim volumes have emerged in this and other procedural specialties—versions of the sincerest form of flattery.

Even so, changes need to be made. As the evolution and exponential growth of cosmetic dermatology continues, new procedures are created, and multiple variants of existing drugs, devices, and techniques emerge. The volumes in the series have been updated to reflect these advances so that the books are now better but remain concise and highly practical.

We are also cognizant of the decline of paper publishing. To preserve the environment and provide content everywhere, all the time, and on all types of media, the series will be available in whole and

chapter-by-chapter in various electronic formats and on several platforms. We have expanded the video offerings because they are worth many pages of text and are easier to follow.

As always, we are very grateful to our chapter book editors and authors. These practitioners are among the most prominent, bright, erudite, and skilled in the world. They have worked tirelessly to provide a uniform tone and structure. It is our hope that you find that these multiauthored books read like a single person wrote them, whose writing is a paragon of clarity.

Our thanks are also due to Elsevier, our publisher since the start. Elsevier has provided our rapid publishing window, which allows content to be put out and disseminated before it goes out of date.

Finally, thanks to you, the reader, for continuing to use these texts. We wish you the joy of learning something new and then delighting your patients with your freshly honed skills.

Jeffrey S. Dover, MD, FRCPC
Murad Alam, MD, MSCI

CHEMICAL PEELS, THIRD EDITION

It is with much excitement that I bring to you the third edition of *Chemical Peels*! This latest textbook on peels will take your knowledge to the next level, building on what was covered in previous editions. Chemical peels will be covered by experts recognized worldwide for their innovation, talent, and skills. This international group of thought leaders will cover the entire approach to the skin resurfacing patient from evaluation, to skin preparation, to performing peels ranging from light peels to the advanced deep peels, and finally to recognizing and managing complications. The new edition features many new chapters dedicated to an in-depth dive into a specific peel or skin condition. These new chapters include trichloroacetic acid (TCA) peels of the chest, neck, and upper extremities; peels as an adjuvant treatment of acne; chemical peels in male patients; several chapters on unique approaches to acne scars; a chapter on combining peels with surgical procedures; and several chapters that illustrate safely performing deeper, modified phenol peels with wonderful photographs to accompany the text. Videos of various procedures will allow easy incorporation of chemical peeling techniques into your practice.

Once again, chemical peels have shown themselves to be time-proven methods with unparalleled flexibility in their performance. Chemical peels have resurged in popularity as courses and didactic sessions are once again being offered to physicians. With a growing,

ethnically diverse population, we need a tool such as chemical peels to allow us to treat every patient with any skin type that comes to us seeking cosmetic enhancement.

I am truly humbled and grateful to work with colleagues from all over the world on this edition, and I thank them for their hard work in bringing to you an exceptional textbook. I want to also recognize and give special thanks to Meghan Address at Elsevier for the patience and guidance she offered all the authors. Furthermore, our series editors, Murad Alam, MD, and Jeffrey Dover, MD, deserve special recognition for their tireless efforts in creating a series of textbooks focused on cosmetic dermatology procedures and for their guidance when the content of this book was being developed.

Lastly, to my family, thank you, thank you, thank you! It was a busy year to say the least, but knowing I had your support made it all worthwhile! I survived many weekends and evenings of writing and editing but made sure to get to all the important family celebrations and school achievements. It was worth the effort!

I hope, as you read through this textbook, your interest in peels is kindled and your desire to hone your skills in this field is heightened. I am sure I speak on behalf of all my coauthors when I say, once a “peeler” always a “peeler.” Hopefully you will join us as a fellow “peeler”!

Sincerely,

Suzan Obagi, MD

LIST OF VIDEOS

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The Chemistry of Peels: A Hypothesis of Mechanism of Action and Classification of Peels

Luc Dewandre, Alain Tenenbaum, Desmer Destang

A chemical peel is a treatment technique used to improve and smooth the facial and/or body skin's texture using a chemical solution that causes the dead skin to slough off and eventually peel off. The regenerated skin is usually smoother, healthier, and less wrinkled than the old skin.

It is advised to seek training with a specialist such as a dermatologist, plastic surgeon, otorhinolaryngologist (facial plastic surgeon), or oral-maxillofacial surgeon who is experienced in the specific types of peels you wish to perform.

INTRODUCTION

This chapter proposes a classification of chemical peels based on the mechanism of action of chemical peel solutions. The traditionally accepted mechanism has been based on the concept that the effect of a peeling solution on the skin is based purely on its acidity. By using elementary concepts in chemistry, three separate mechanisms of action for chemical peeling solutions are explained:

1. Acidity
2. Toxicity
3. Metabolic interactions

The literature devoted to chemical peels is full of information about the methodology, indications, contraindications, side effects, and results obtained. Without any proof, acidity has always been assumed to be the sole mechanism of action of peeling agents. All peeling agents were assumed to induce the three stages of tissue

replacement: destruction, elimination, and regeneration, all accompanied by a controlled stage of inflammation.

A brief study of the chemistry of the molecules and solutions used in chemical peels immediately questions the hypothesis that acidity is the only basis for the action of peeling solutions. In fact, with the exception of trichloroacetic acid (TCA) and nonneutralized glycolic acid solutions, the most commonly used peeling solutions are only weakly acidic, and phenol and resorcinol mixtures may not be acidic at all, having a pH greater than 7 in some formulations.

This chapter will discuss the elementary chemistry concepts that, along with a review of the chemistry of the skin, should help explain the possible interactions between different peeling solutions and the skin. Finally, two classifications of solutions for peelings will be proposed, one according to their mechanisms of action (classification of L. Dewandre) and the other according to chemical parameters (structure of the molecule, pK_a , etc; or classification of A. Tenenbaum).

USEFUL ELEMENTS OF BASIC CHEMISTRY

Understanding some of the basic concepts of chemistry is necessary to truly understand chemical peels. Mineral and organic chemistry are taught as biochemistry to medical students, but most practicing physicians do not remember these fundamental principles.

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Also chemistry has been unfortunately neglected in cosmetic dermatology and aesthetic medicine courses, masters workshops, and congresses. A brief review of useful information should help update most practitioners.

Acids

An acid (from the Latin *acidus*, meaning “sour”) is traditionally considered any chemical compound that, when dissolved in water, gives a solution with a hydrogen ion activity greater than in pure water, i.e., a pH less than 7.0. That approximates the modern definition of Johannes Nicolaus Brønsted and Martin Lowry, who independently defined an acid as a compound that donates a hydrogen ion (H^+) to another compound (called a *base*). Acid–base systems are different from redox reactions in that there is no change in oxidation state. Acids can occur in solid, liquid, or gaseous form, depending on the temperature. They can exist as pure substances or in solution. Chemicals or substances having the property of an acid are said to be acidic (adjective).

Arrhenius Acids

The Arrhenius concept is the easiest one retained by most peelers, because most peeling acids are ionic compounds, acting as a source of H_3O^+ when dissolved in water.

The Swedish chemist Svante Arrhenius attributed the properties of acidity to hydrogen in 1884. An Arrhenius acid is a substance that increases the concentration of the hydronium ion, H_3O^+ , when dissolved in water. This definition stems from the equilibrium dissociation of water into hydronium and hydroxide (OH^-) ions:



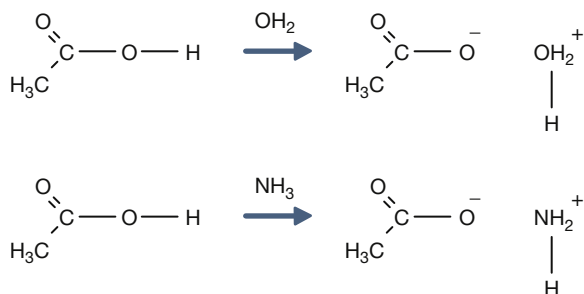
In pure water most molecules exist as H_2O , but a small number of molecules are constantly dissociating and reassociating. Pure water is neutral with respect to acidity or basicity, because the concentration of hydroxide ions is always equal to the concentration of hydronium ions. An Arrhenius base is a molecule that increases the concentration of the hydroxide ion when dissolved in water. Note that chemists often write $\text{H}^+(\text{aq})$ and refer to the hydrogen ion when describing acid–base reactions, but the free hydrogen nucleus, a proton, does not exist alone in water; it exists as the hydronium ion, H_3O^+ .

Brønsted Acids

Although the Arrhenius concept is useful for describing many reactions, it is also quite limited in its scope. Brønsted acids act by donating a proton to water and,

differently than Arrhenius acids, can also be used to describe molecular compounds, whereas Arrhenius acids must be ionic compounds.

In 1923 chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently recognized that acid–base reactions involve the transfer of a proton. A Brønsted–Lowry acid (or simply Brønsted acid) is a species that donates a proton to a Brønsted–Lowry base. Brønsted–Lowry acid–base theory has several advantages over Arrhenius theory. Consider the following reactions of acetic acid (CH_3COOH) (used as a chemical peel for the *décolleté* by some great peelers like L. Wiest), the organic acid that gives vinegar its characteristic taste:



Both theories easily describe the first reaction: CH_3COOH acts as an Arrhenius acid because it acts as a source of H_3O^+ when dissolved in water, and it acts as a Brønsted acid by donating a proton to water. In the second example CH_3COOH undergoes the same transformation, donating a proton to ammonia (NH_3), but it cannot be described using the Arrhenius definition of an acid because the reaction does not produce hydronium.

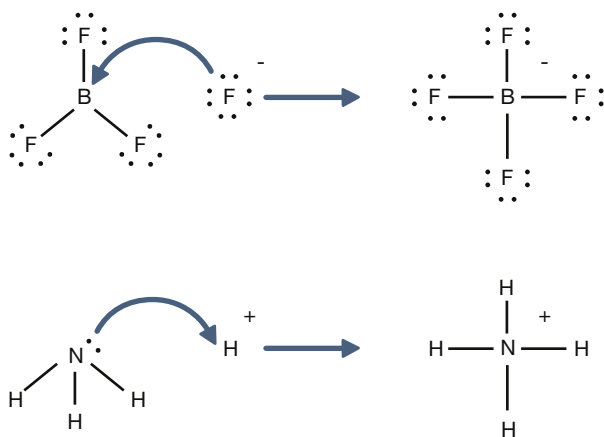
As with the acetic acid reactions, both definitions work for the first example, where water is the solvent and a hydronium ion is formed. The next reaction does not involve the formation of ions but can still be viewed as a proton transfer reaction.

Lewis Acids

The Brønsted–Lowry definition is the most widely used definition; unless otherwise specified, acid–base reactions are assumed to involve the transfer of a proton (H^+) from an acid to a base.

A third concept was proposed by Gilbert N. Lewis that includes reactions with acid–base characteristics that do not involve a proton transfer. A Lewis acid is a species that accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid–base reactions are proton transfer reactions,

whereas Lewis acid–base reactions are electron pair transfers. All Brønsted acids are also Lewis acids, but not all Lewis acids are Brønsted acids. Contrast the following reactions, which could be described in terms of acid–base chemistry:



In the first reaction a fluoride ion, F^- , gives up an electron pair to boron trifluoride to form the product tetrafluoroborate. Fluoride “loses” a pair of valence electrons because the electrons shared in the B–F bond are located in the region of space between the two atomic nuclei and are therefore more distant from the fluoride nucleus than they are in the lone fluoride ion. BF_3 is a Lewis acid because it accepts the electron pair from fluoride. This reaction cannot be described in terms of Brønsted theory, because there is no proton transfer. The second reaction can be described using either theory. A proton is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion. The species that gains the electron pair is the Lewis acid; for example, the oxygen atom in H_3O^+ gains a pair of electrons when one of the H–O bonds is broken and the electrons shared in the bond become localized on oxygen. Depending on the context, Lewis acids may also be described as a reducing agent or an electrophile.

Dissociation and Equilibrium

Reactions of acids are often generalized in the form $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, where HA represents the acid and A^- is the conjugate base. Acid–base conjugate pairs differ by one proton and can be interconverted by the addition or removal of a proton (protonation and deprotonation,

respectively). Note that the acid can be the charged species and the conjugate base can be neutral, in which case the generalized reaction scheme could be written as $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}$. In solution there exists an equilibrium between the acid and its conjugate base. The equilibrium constant K is an expression of the equilibrium concentrations of the molecules or the ions in solution. Brackets indicate concentration, such that $[\text{H}_2\text{O}]$ means the concentration of H_2O . The acid dissociation constant K_a is generally used in the context of acid–base reactions. The numerical value of K_a is equal to the concentration of the products divided by the concentration of the reactants, where the reactant is the acid (HA) and the products are the conjugate base and H^+ .

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The stronger of two acids will have a higher K_a than the weaker acid; the ratio of hydrogen ions to acid will be higher for the stronger acid because the stronger acid has a greater tendency to lose its proton. Because the range of possible values for K_a spans many orders of magnitude, a more manageable constant, $\text{p}K_a$, is more frequently used, where $\text{p}K_a = -\log_{10}K_a$. Stronger acids have a smaller $\text{p}K_a$ than weaker acids. Experimentally determined $\text{p}K_a$ at 25°C in aqueous solution are often quoted in textbooks and reference material.

Acid Strength

For peelers, the notion of acid strength is very important, because stronger acids have a higher K_a and a lower $\text{p}K_a$ than weaker acids.

For our classification, two parameters have to be taken into consideration for peelers:

1. The $\text{p}K_a$, a synonym of the acid’s strength.
2. The pH, a synonym of the penetration for the selected acid.

For chemists, the strength of an acid refers to its ability or tendency to lose a proton. A strong acid is one that completely dissociates in water; in other words, one mole of a strong acid, HA, dissolves in water, yielding one mole of H^+ and one mole of the conjugate base, A^- , and none of the protonated acid HA. In contrast a weak acid only partially dissociates, and at equilibrium both the acid and the conjugate base are in solution. In water each of these essentially ionizes 100%. The stronger an

acid is, the more easily it loses a proton, H^+ . Two key factors that contribute to the ease of deprotonation are the polarity of the $\text{H}-\text{A}$ bond and the size of atom A, which determines the strength of the $\text{H}-\text{A}$ bond. Acid strengths are also often discussed in terms of the stability of the conjugate base.

Caution is advised against simply classifying “cosmetic peels” for acids with $\text{p}K_{\text{a}} > 3$ and “medical peels” for acids with $\text{p}K_{\text{a}} < 3$, because some acids like phenol can be toxic substances even with a $\text{p}K_{\text{a}} > 3$.

Polarity and the Inductive Effect

The polarity of the $\text{H}-\text{A}$ bond is the first factor contributing to acid strength.

As the electron density on hydrogen decreases, it becomes more acidic. Moving from left to right across a row on the periodic table, elements become more electronegative (excluding the noble gases).

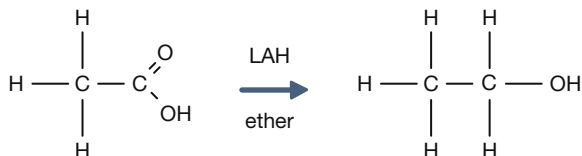
In several compound classes, collectively called *carbon acids*, the $\text{C}-\text{H}$ bond can be sufficiently acidic for proton removal. Inactivated $\text{C}-\text{H}$ bonds are found in alkanes and are not adjacent to a heteroatom (O, N, Si, etc.). Such bonds usually only participate in radical substitution.

Polarity refers to the distribution of electrons in a bond, the region of space between two atomic nuclei where a pair of electrons is shared. When two atoms have roughly the same electronegativity (ability to attract electrons), the electrons are shared evenly and spend equal time on either end of the bond. When there is a significant difference in electronegativities of two bonded atoms, the electrons spend more time near the nucleus of the more electronegative element and an electrical dipole, or separation of charges, occurs, such that there is a partial negative charge localized on the electronegative element and a partial positive charge on the electropositive element. Hydrogen is an electropositive element and accumulates a slightly positive charge when it is bonded to an electronegative element such as oxygen or chlorine.

The electronegative element need not be directly bonded to the acidic hydrogen to increase its acidity. An electronegative atom can pull electron density out of an acidic bond through the inductive effect. The electron-withdrawing ability diminishes quickly as the electronegative atom moves away from the acidic bond.

Carboxylic acids are organic acids that contain an acidic hydroxyl group and a carbonyl ($\text{C}=\text{O}$ bond).

Carboxylic acids can be reduced to the corresponding alcohol; the replacement of an electronegative oxygen atom with two electropositive hydrogens yields a product that is essentially nonacidic. The reduction of acetic acid to ethanol using LiAlH_4 (lithium aluminum hydride or LAH), and ether is an example of such a reaction.



The $\text{p}K_{\text{a}}$ for ethanol is 16, compared with 4.76 for acetic acid.

Atomic Radius and Bond Strength

The size of the atom A or atomic radius is the second factor contributing to acid strength.

Moving down a column on the periodic table, atoms become less electronegative but also significantly larger, and the size of the atom tends to dominate its acidity when sharing a bond to hydrogen.

Hydrogen sulfide, H_2S , is a stronger acid than water, even though oxygen is more electronegative than sulfur. This is because sulfur is larger than oxygen and the $\text{H}-\text{S}$ bond is more easily broken than the $\text{H}-\text{O}$ bond.

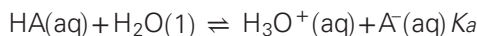
Another factor that contributes to the ability of an acid to lose a proton is the strength of the bond between the acidic hydrogen and the atom that bears it. This, in turn, is dependent on the size of the atoms sharing the bond. For an acid HA , as the size of atom A increases, the strength of the bond decreases, meaning that it is more easily broken, and the strength of the acid increases.

Chemical Characteristics

It is important to keep in mind the difference between monoprotic acids (having one unique $\text{p}K_{\text{a}}$) and polyprotic acids (having two or more $\text{p}K_{\text{a}}$).

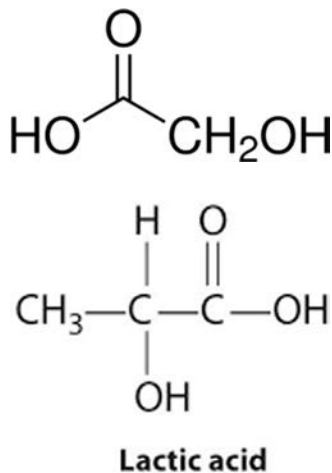
Monoprotic Acids

Monoprotic acids are those acids that are able to donate one proton per molecule during the process of dissociation (sometimes called *ionization*), as shown below (symbolized by HA):



Common examples of monoprotic acids in organic acids indicate the presence of one carboxyl group,

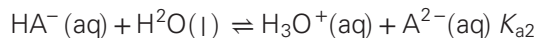
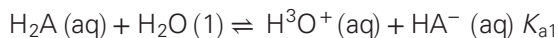
and mostly these acids are known as monocarboxylic acid. Examples in organic acids include acetic acid (CH_3COOH), glycolic acid, and lactic acid.



Polyprotic Acids

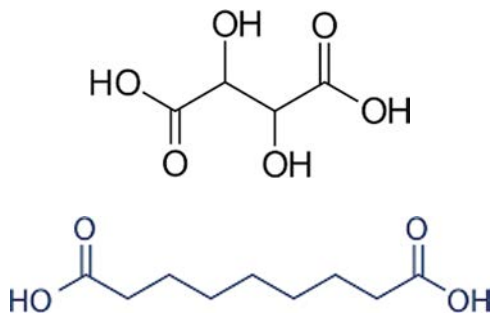
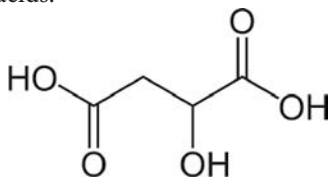
Polyprotic acids are able to donate more than one proton per acid molecule, in contrast to monoprotic acids that only donate one proton per molecule. Specific types of polyprotic acids have more specific names, such as diprotic acid (two potential protons to donate) and triprotic acid (three potential protons to donate).

A diprotic acid (here symbolized by H_2A) can undergo one or two dissociations depending on the pH. Each dissociation has its own dissociation constant, K_{a1} and K_{a2} .



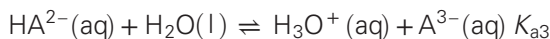
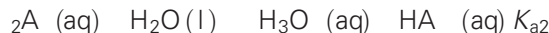
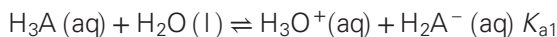
The first dissociation constant is typically greater than the second; i.e., $K_{a1} > K_{a2}$. For example, the weak unstable carbonic acid (H_2CO_3) can lose one proton to form bicarbonate anion (HCO_3^-) and lose a second to form carbonate anion (CO_3^{2-}). Both K_a values are small, but $K_{a1} > K_{a2}$.

Diprotic acids used for peels are malic, tartaric, and azelaic acids.

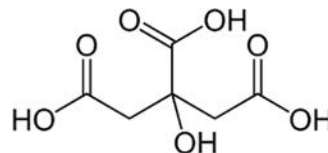


Two dissociations mean that such acids can generate two peelings, depending on the pH, with the second one less acidic than the first one. In this case, we consider one peeling reaction per one dissociation.

A triprotic acid (H_3A) can undergo one, two, or three dissociations and has three dissociation constants, where $K_{a1} > K_{a2} > K_{a3}$.



An organic example of a triprotic acid is citric acid, which can successively lose three protons to finally form the citrate ion. Even though the positions of the protons on the original molecule may be equivalent, the successive K_a values will differ, because it is energetically less favorable to lose a proton if the conjugate base is more negatively charged.



Weak Acid–Weak Base Equilibria

To lose a proton, it is necessary that the pH of the system rise above the $\text{p}K_a$ of the protonated acid. The decreased concentration of H^+ in that basic solution shifts the equilibrium toward the conjugate base form (the deprotonated form of the acid). In lower-pH (more acidic) solutions, there is a high enough H^+ concentration in the solution to cause the acid to remain in its protonated

form, or to protonate its conjugate base (the deprotonated form).

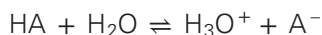
Solutions of weak acids and salts of their conjugate bases form buffer solutions.

Buffer Solution

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. The property of buffer solutions is that the pH of the solution changes very little when a small amount of acid or base is added to it. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. Many life forms thrive only in a relatively small pH range; an example of a buffer solution is blood.

Le Chatelier's Principle

In a solution there is an equilibrium between a weak acid, HA, and its conjugate base, A⁻:



- When hydrogen ions (H⁺) are added to the solution, equilibrium moves to the left, as there are hydrogen ions (H⁺ or H₃O⁺) on the right-hand side of the equilibrium expression.
- When hydroxide ions (OH⁻) are added to the solution, equilibrium moves to the right, as hydrogen ions are removed in the reaction (H⁺ + OH⁻ → H₂O).

Thus, in both cases, some of the added reagent is consumed in shifting the equilibrium in accordance with Le Chatelier's principle, and the pH changes by less than it would if the solution were not buffered.

Henderson–Hasselbach Equation

The acid dissociation constant for a weak acid, HA, is defined as:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Simple manipulation with logarithms gives the Henderson–Hasselbach equation, which describes pH in terms of pK_a:

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

In this equation [A⁻] is the concentration of the conjugate base and [HA] is the concentration of the acid. It follows that when the concentrations of acid and conjugate base are equal, often described as half-neutralization, pH = pK_a. In general, the pH of a buffer solution may be easily calculated, knowing the composition of the mixture, by means of an ICE table. An ICE (initial, change, equilibrium) table is a simple matrix formalism that used to simplify the calculations in reversible equilibrium reactions (e.g., weak acids and weak bases or complex ion formation).

One should remember that the *calculated* pH may be different from *measured* pH.

Buffer Capacity

Buffer capacity (Fig. 1.1) is a quantitative measure of the resistance of a buffer solution to pH change with the addition of hydroxide ions. It can be defined as follows:

$$\text{Buffer capacity} = \frac{dn}{d(\text{pH})}$$

where dn is an infinitesimal amount of added base and d(pH) is the resulting infinitesimal change in pH. With this definition the buffer capacity can be expressed as:

$$\frac{dn}{d(\text{pH})} = 2.303 \left(\frac{K_w}{[\text{H}^+]} + [\text{H}^+] + \frac{C_A K_a [\text{H}^+]}{(K_a + [\text{H}^+])^2} \right)$$

where K_w is the self-ionization constant of water and C_A is the analytical concentration of the acid, equal to [HA] + [A⁻]. The term K_w/[H⁺] becomes significant at pH greater than about 11.5, and the second term becomes significant at pH less than about 2. Both these terms are properties of water and are independent of the weak acid. Considering the third term, it follows that:

1. Buffer capacity of a weak acid reaches its maximum value when pH = pK_a.
2. At pH = pK_a ± 1 the buffer capacity falls to 33% of the maximum value. This is the approximate range within which buffering by a weak acid is effective. Note: at pH = pK_a - 1, the Henderson–Hasselbach equation shows that the ratio [HA]:[A⁻] is 10:1.
3. Buffer capacity is directly proportional to the analytical concentration of the acid.

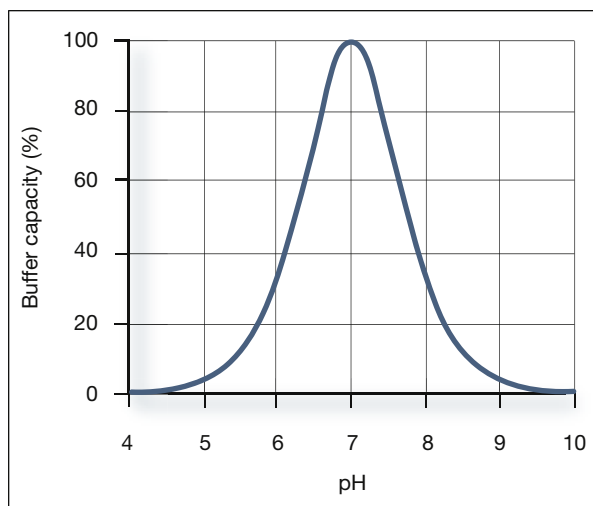


Fig. 1.1 Buffer capacity for $pK_a = 7$ as a percentage of maximum.

Current Applications of Buffer Solutions

Their resistance to changes in pH makes buffer solutions very useful for chemical manufacturing and essential for many biochemical processes. The ideal buffer for a particular pH has a pK_a equal to that pH, since such a solution has maximum buffer capacity.

Buffer solutions are necessary to keep the correct physiological pH for enzymes in many organisms to work. A buffer of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) is present in blood plasma, to maintain a pH between 7.35 and 7.45.

The majority of biological samples used in research are made in buffers, specifically phosphate-buffered saline (PBS) at pH 7.4.

Buffered TCA are more likely to create dyschromias.

Useful Buffer Mixtures

- Citric acid, sodium citrate, pH range 2.5 to 5.6.
- Acetic acid, sodium acetate, pH range 3.7 to 5.6.

Neutralization

There is among physicians a big confusion between a buffered peel (see above) and a neutralized peel. In chemistry, neutralization is a chemical reaction whereby an acid and a base react to form water and a salt.

In an aqueous solution, solvated hydrogen ions (hydronium ions, H_3O^+) react with hydroxide ions (OH^-) formed from the alkali to make two molecules

of water. A salt is also formed. In nonaqueous reactions, water is not always formed; however, there is always a donation of protons (see Brønsted–Lowry acid–base theory).

Often, neutralization reactions are exothermic, giving out heat to the surroundings (the enthalpy of neutralization). On the other hand, an example of endothermic neutralization is the reaction between sodium bicarbonate (baking soda) and any weak acid—for example, acetic acid (vinegar).

Neutralization of the chemical peeling agent is an important step, the timing of which is determined by either the frost in the skin or how much contact time the peel has with the skin. Neutralization is achieved by a majority of peelers applying cold water or wet, cool towels to the face following the frost. According to physical chemistry, using water just after the frost provokes an exothermic reaction that can provoke a “cold” burn. Other neutralizing agents that can be used include bicarbonate spray or soapless cleansers. Peeling agents for which this neutralization step is less important include salicylic acid, Jessner’s solution, TCA, and phenol.

In partially neutralized alpha-hydroxy acid (AHA) solutions, the acid and a lesser amount of base are combined in a reversible chemical reaction that yields unneutralized acid and a salt.

The resulting solution has less free acid and a higher pH than a solution that has not been neutralized. In partially neutralized formulations, the salt functions as a reservoir of acid that is available for second-phase penetration. This means that partially neutralized formulas can deliver as much, if not more, AHA than free acid formulas, but in a safer, “time-released” manner. Therefore the use of partially neutralized glycolic acid solutions seems prudent, because they have a better safety profile than low-pH solutions containing only free glycolic acid.

Clinical studies have shown that a partially neutralized lactic acid preparation improves the skin, both in appearance and histologically. Other studies using skin tissue cultures showed that partially neutralized glycolic acid stimulates fibroblast proliferation—an index of tissue regeneration. Looking at electrical conductance of the skin (an indicator of water content or moisturization), higher pH products (those that have been partially neutralized) are better moisturizers than lower pH preparations.

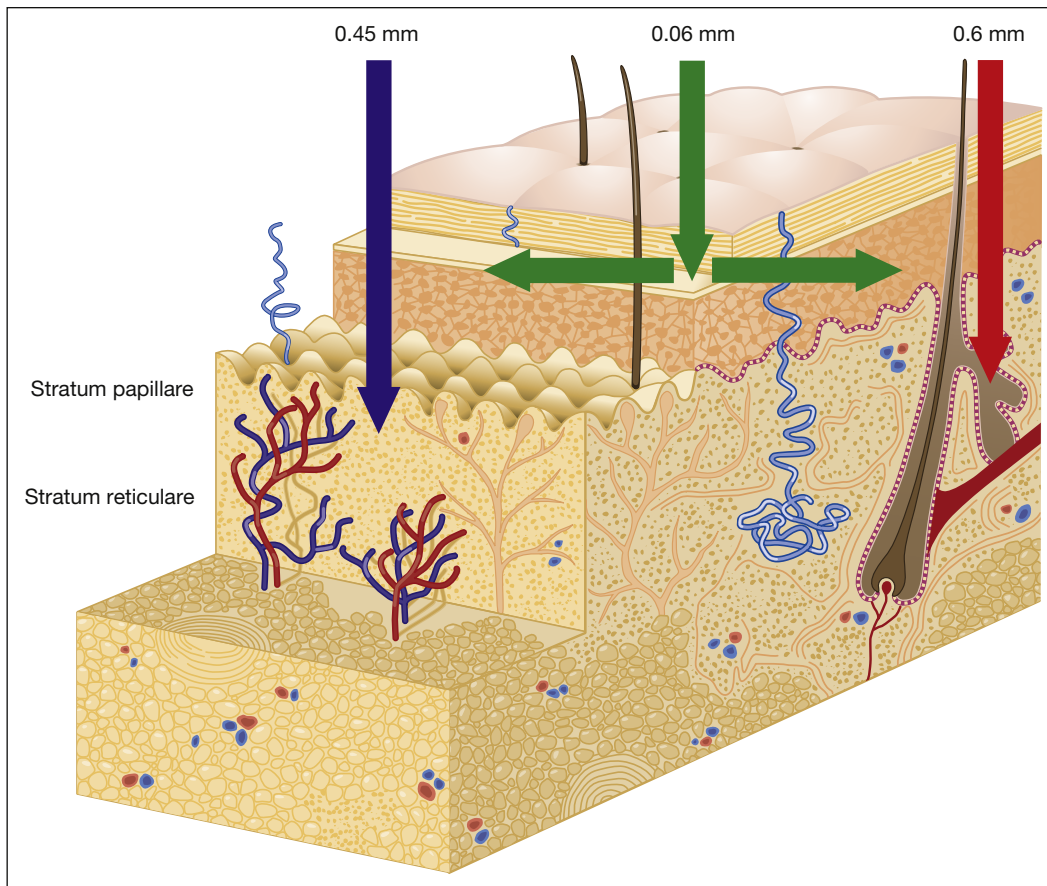


Fig. 1.2 Anatomy of the skin with penetration depths of the various peels: *green*, superficial peels; *blue*, medium-depth peels; and *red*, deep peels.

ANATOMY OF THE SKIN

Like the whole human organism, the skin can be considered an aqueous solution into which are dissolved a certain number of molecules (Fig. 1.2). These are molecules of proteins, lipids, and carbohydrates in variable quantities and proportions.

There is more water in the dermis than in the epidermis. This is due to the presence of blood, glycosaminoglycans (GAGs), and lymph in the dermis, all of which have a high water content, as well as the fact that the epidermis is in contact with a more or less dehydrated environment.

There are more proteins (keratin) in the epidermis than in the dermis, whereas more carbohydrates and lipids exist in the dermis, and there are even more in the subcutaneous layer than in the dermis.

The most important molecule in the epidermis is a fibrous and corneal protein, keratin, that protects and takes part, through its continuous production by the keratinocytes, in the complete replacement of the epidermis every 27 days.

The most important molecules of the dermis are collagen, elastin, GAGs, and the proteoglycans. Collagen and elastin are proteins, whereas GAGs (e.g., hyaluronic acid) and the proteoglycans are biological polymers formed mainly by sugars that retain water.

Collagen constitutes the skin's structural resource and is the most abundant protein in the human body. It is formed mainly by glycine, proline, and hydroxyproline. It is one of the most resistant natural proteins and helps give the skin structural support. Elastin is similar to collagen, but it is an extensible protein responsible for

elasticity; hence its name. It has two unique polypeptides, desmosine and isodesmosine.

The GAGs contain specific sugars such as glucosamine sulfate, *N*-acetylglucosamine, and glucosamine hydrochloride, all very capable of attracting water. They form long chains of molecules, such as hyaluronic acid, keratin sulfate, heparin, dermatin, and chondroitin, that retain up to 1000 times their weight in water.

The hypodermis or subcutaneous tissue consists mainly of fat, although this tissue accounts for a completely different chemical interaction with peeling solutions. Chemical peels are not meant to extend down into the subcutaneous layer, so this is not discussed.

The different molecular composition of the different levels of the skin may explain the variability of the interactions and the results obtained. These benefits are correlated to the penetration level achieved when using a given peeling agent.

It is likewise for the pH. Although the pH of the epidermis is a well-established number, the pH of the dermis is not an exact value and has been difficult to measure precisely.

The epidermal acid layer or *mantel* is the result of sebum secretion and sweat. It protects the skin and makes it less vulnerable from attacks by microorganisms such as bacteria and fungi. A healthy epidermis has a slightly acidic pH with a range between 4.2 and 5.6. It varies from one part of the skin to another and, in general, is more acidic in men than in women.

The pH of the epidermis also varies depending on its different layers. For a “skin” pH of around 5 we will find a pH near 5.6 in the corneal layer and one of 4.8 in the deep layers of the epidermis, which are rich in corneocytes and melanocytes. Finally, dry skin is more acidic than oily skin, which can reach pH 6.

Because the dermis contains a significant amount of fluid and blood, we can presume the pH to be 6 to 6.5, and it is slightly less acidic than the epidermis, with a pH of 6 for the papillary dermis and 7 for the vascular reticular dermis.

Skin Basic Chemistry

The approximate skin composition is seen in [Box 1.1](#).

Acids and Cell Membranes

Cell membranes contain fatty acid esters such as phospholipids. Fatty acids and fatty acid derivatives

BOX 1.1 Approximate Skin Composition

Water 70%
Proteins 25.5%
Lipids 2.0%
Oligo mineral elements 0.5% (e.g., zinc, copper, selenium)
Carbon hydrates 2.0% (mucopolysaccharides)

are another group of carboxylic acids that play a significant role in biology. These contain long hydrocarbon chains and a carboxylic acid group on one end. The cell membrane of nearly all organisms is primarily made up of a phospholipid bilayer, a micelle of hydrophobic fatty acid esters with polar, hydrophilic phosphate “head” groups. Membranes contain additional components, some of which can participate in acid–base reactions. Cell membranes are generally impermeable to charged or large, polar molecules because of the lipophilic fatty acyl chains comprising their interior. Many biologically important molecules, including a number of pharmaceutical agents, are organic weak acids that can cross the membrane in their protonated, uncharged form but not in their charged form (i.e., as the conjugate base). The charged form, however, is often more soluble in blood and cytosol, both aqueous environments. When the extracellular environment is more acidic than the neutral pH within the cell, certain acids will exist in their neutral form and will be membrane soluble, allowing them to cross the phospholipid bilayer. Acids that lose a proton at the intracellular pH will exist in their soluble, charged form and are thus able to diffuse through the cytosol to their target.

BASIC CHEMISTRY OF THE MOST USED MOLECULES IN SOLUTIONS FOR CHEMICAL PEELINGS

It is interesting to consider the chemical nature of the molecules most commonly found in chemical peels. In the case of the alpha-hydroxy acids, the acid carboxyl group is on the first carbon (C1) and the hydroxyl is on the alpha carbon (C2). Salicylic acid is a beta-hydroxy acid with the hydroxyl group on C3.

How the Most Commonly Used Substances in Chemical Peel Solutions Work—A

Hypothesis

Based on their different properties and the ways in which they work, L. Dewandre divides the substances most used for chemical peels into three categories: metabolic, caustic, and toxic (Table 1.1).

SUBSTANCES WITH MAINLY METABOLIC ACTIVITY

With the exception of glycolic and lactic acids, the metabolic substances described in the following sections are not used, properly speaking, in the solutions involved in chemical peels. Today, glycolic and lactic acids are nearly ubiquitous in medical cosmetology as a part of skin care regimens and in the office as chemical peel procedures.

Alpha Hydroxy Acids

The AHAs are a class of chemical compounds that consist of a carboxylic acid with a hydroxy group on the adjacent carbon. They may be either naturally occurring or synthetic. AHAs are well known for their use in the cosmetics industry. They are often found in products claiming to reduce wrinkles or the signs of aging and improve the overall look and feel of the skin. They are also used as chemical peels available in a dermatologist's office, beauty and health spas, and home kits, which usually contain a lower concentration. Although their effectiveness is documented, numerous cosmetic products have appeared on the market with unfounded claims of performance. Many well-known AHAs are useful building blocks in organic synthesis: the most common and simple are glycolic acid, lactic acid, citric acid, and mandelic acid.

AHA peels include aliphatic (lactic, glycolic, tartaric, and malic) and aromatic (mandelic) acids that are synthesized chemically for use in peels. Various concentrations can be purchased, with 10% to 70% concentration used for facial peels, most commonly 50% or 70%. AHAs are weak acids that induce their rejuvenation activity by either metabolic or caustic effect. At low concentration (<30%), they reduce sulfate and phosphate groups from the surface of corneocytes. By decreasing corneocyte cohesion, they induce exfoliation of the epidermis. At higher concentration, their effect is mainly destructive. Because of the low acidity of AHAs, they do not induce

enough coagulation of the skin proteins and therefore cannot neutralize themselves. They must be neutralized using a weak buffer.

Knowledge of the skin structure within the framework of cutaneous aging is helpful to understand the topical action of AHAs. Human skin has two principal components, the avascular epidermis and the underlying vascular dermis. Cutaneous aging, though it has epidermal involvement, seems to involve primarily the dermis and is caused by both intrinsic and extrinsic aging factors.

AHAs most commonly used in cosmetic applications are typically derived from fruit products including glycolic acid (sugar cane), lactic acid (sour milk), malic acid (apples), citric acid (citrus fruits) and tartaric acid (grapes and wine). For any topical compound, including AHA, it must penetrate into the skin, where it can act on living cells. Bioavailability (influenced primarily by small molecular size) is one characteristic that is important in determining the compound's ability to penetrate the top layer of the skin. Glycolic acid having the smallest molecular size is the AHA with greatest bioavailability and penetrates the skin most easily; this largely accounts for the popularity of this product in cosmetic applications.

- *Epidermal effects:* AHAs have a profound effect on keratinization, which is clinically detectable by the formation of a new stratum corneum. It appears that AHAs modulate this formation through diminished cellular cohesion between corneocytes at the lowest levels of the stratum corneum.
- *Dermal effects:* AHAs with greater bioavailability appear to have deeper dermal effects. Glycolic acid, lactic acid, and citric acid, on topical application to photodamaged skin, have been shown to produce increased amounts of mucopolysaccharides and collagen and increased skin thickness without detectable inflammation, as monitored by skin biopsies.

AHAs are generally safe when used on the skin as a cosmetic agent using the recommended dosage. The most common side effects are mild skin irritation, redness, and flaking. The severity usually depends on the pH and the concentration of the acid used.

The Food and Drug Administration (FDA) has also warned consumers that care should be taken when using AHAs after an industry-sponsored study found that they can increase photosensitivity to the sun.

TABLE 1.1 Classification of Chemical Peels (A. Tenenbaum)

Acids Category	Acids Subcategory	$pK_a > 3$ from Lower to Higher	$pK_a = 3$	$pK_a < 3$	pK_{a1}	pK_{a2}	pK_{a3}	Classification of L. Dewandre	Number of Reactions
Alpha hydroxy	Aliphatic		Tartaric		3.04	4.37		Metabolic	Diprotic
		Citric			3.15	4.77	6.40	Metabolic	Triprotic
		Malic			3.40	5.13		Metabolic	Diprotic
		Glycolic			3.83			Metabolic	Monoprotic
	Aromatic	Lactic	Mandelic		3.86			Metabolic	Monoprotic
					3.37			Metabolic	Monoprotic
		TXA			4.3				Monoprotic
				Pyruvic	2.49			Not available	Monoprotic
Alpha keto									
Bicarboxylic		Azelaic			4.55	5.59		Metabolic	Diprotic
Beta Hydroxy			Salicylic		2.97			Toxic	Monoprotic
TCA				TCA	0.53			Caustic	Monoprotic
Phenol	Aromatic	Phenol			9.95			Toxic	Alcohol > acid

TCA, Trichloroacetic acid; TXA, tranexamic acid.

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Exploring the Variety of Random Documents with Different Content

for us," said one of the apologists of the early ages, "we make little difference between committing murder and seeing it committed."²¹

CHAPTER XXXII.

THE IMPROVEMENT OF MANNERS BY THE ACTION OF THE CHURCH.

Modern society ought, it would seem, to be distinguished for severity and cruelty, since it was formed from that of the Romans and barbarians, from both of whom it should have inherited these qualities. Who is not aware of the fierce manners of the northern barbarians? The historians of that time have left us statements that make us shudder when we read them. It was believed that the end of the world was at hand; and, indeed, it was excusable to consider the last catastrophe as near, when so many other melancholy ones had already been heaped upon humanity. The imagination cannot figure to itself what would have happened to the world at this crisis, if Christianity had not existed. Even supposing that society would have been organized anew under one form or another, it is certain that private and public relations would have remained in a state of lamentable disorder, and that legislation would have been unjust and inhuman. Thus the influence of the Church on civil legislation was an inestimable benefit; thus even the power of the clergy in temporal things was one of the greatest safeguards of the highest interests of society.

Attacks are often made upon this temporal power of the clergy and this influence of the Church in worldly affairs. But, in the first place, it should be remembered, that this power and influence were brought about by the very nature of things; that is to say, they were natural, and, consequently, to assail them is to declaim in vain against the force of events, of which no man could hinder the realization. This power and influence, besides, were legitimate; for

when society is in danger, nothing can be more legitimate than that that which can save it should save it. Now, at the time we speak of, the Church alone could save society. The Church, which is not an abstract being, but a real and substantial society, acted upon civil society by real and substantial means. If the purely material interests of society were in question, the minister of the Church ought, in some way or other, to take part in the direction of those interests. These reflections are so natural and simple, that their truth must be seen by good sense. All those who know any thing of history are now generally agreed on this point; and if we are not aware how much it generally costs the human mind to enter upon the path of truth, and, above all, how much bad faith there has been in the examination of these questions, we shall have a difficulty in understanding that so much time should have been required to bring the world to agree on a thing which is apparent to those who read history. But let us return to our subject. This extraordinary mixture of the cruelty of a cultivated but corrupted people with the atrocious ferocity of a barbarous one, proud of its triumphs, and intoxicated with blood during long wars, placed in European society a germ of severity and cruelty which fermented there for ages, and the remains of which we find at a late period. The precept of Christian charity was in men's heads, but Roman cruelty and barbarian ferocity still prevailed in their hearts; ideas were pure and beneficent, since they proceeded from a religion of love, but they encountered a terrible resistance in the habits, manners, institutions, and laws, for all these were more or less disfigured by the two mixed principles which I have just pointed out. If we reflect upon the constant and obstinate struggle between the Catholic Church and the elements which contended with her, we shall clearly see that Christian ideas could never have prevailed in legislation and manners, if Christianity had been a religious idea abandoned to human caprice, as Protestants imagine; it was necessary for it to be realized in a powerful institution, in a strongly constituted society, such as we find in the Catholic Church. In order to give an idea of the efforts made by the Church, I will point out some of the regulations which she made for the purpose of improving manners.

Private animosities were very violent at the time of which we speak; and right was decided by force, and the world was threatened with becoming the patrimony of the strongest. Public law did not exist, or was hurried away and confounded by outrages which its feeble hand could never prevent or repress; it was altogether powerless in rendering manners pacific, and in subjecting men to reason and justice. Then we see that the Church, besides the instruction and the general admonitions inseparable from her sacred mission, adopted at that time certain measures calculated to restrain the torrent of violence which ravaged and destroyed every thing. The Council of Arles, celebrated in the middle of the fifth century, between 443 and 452, ordains, in its 50th canon, that the Church should be interdicted to those who have public animosities, until they were reconciled. The Council of Angers, celebrated in 453, proscribes, by its 3d canon, acts of violence and mutilation. The Council of Agde, in Languedoc, celebrated in 506, ordains, in its 31st canon, that enemies who would not be reconciled should be admonished by the priests, and excommunicated if they did not follow their apostolical counsels.

The Franks at that time had the custom of going armed, and they always entered the churches with their arms. It will be understood that such a custom must have produced great evils; the house of prayer was often converted into an arena of blood and vengeance. In the middle of the seventh century, the Council of Chalons-sur-Saone, in its 17th canon, pronounces excommunication against all laymen who excite tumults, or draw their swords to strike any one in the churches or in their precincts. Thus, we see the prudence and foresight which dictated the 29th canon of the third Council of Orleans, celebrated in 538, which forbids any one to be present at mass or vespers, armed. It is curious to observe the uniformity of design and plan pursued by the Church. In countries the most distant from each other, and at times when communication could not be frequent, we find regulations analogous to those which we have pointed out. The Council of Lerida, held in 546, ordains, by its 7th canon, that he who shall have sworn not to be reconciled with his enemy, shall be deprived of the participation of the body and blood

of Jesus Christ until he has done penance for his oath and been reconciled.

Centuries passed away, acts of violence continued, the precept of fraternal charity, which obliges us to love even our enemies, always met with open resistance in the harsh character and fierce passions of the descendants of the barbarians; but the Church did not cease to preach the divine command; she continually inculcated and labored to render it efficacious by means of spiritual penalties. More than four hundred years had elapsed since the celebration of the Council of Arles, where we have seen the church forbidden to those who were openly at variance; we then see the Council of Worms, held in 868, pronouncing, in its 41st canon, excommunication against enemies who refused to be reconciled. It will suffice to have some idea of the disorders of that time, to know whether it was possible to appease the violence of animosities during this long period. One would fancy that the Church would have been wearied of inculcating a precept which the unhappy state of circumstances so often rendered fruitless; but such was not the case: she continued to speak as she had spoken for ages; she never lost her confidence that her words would produce fruit in the present, and would be productive in the future. Such is her system; one would think that she heard these words constantly repeated, "Cry out, cry out without ceasing; raise thy voice like a trumpet." It is then that she triumphs over all resistance; when she cannot exert her power over the will of a nation, she makes her voice heard with indefatigable diligence in the sanctuary. There she assembles seven thousand who have not bent the knee to Baal; and while she endeavors to confirm them in faith and good works, she protests, in the name of God, against those who resist the Holy Spirit. Let us imagine that, amid the dissipation and distraction of a populous city, we enter a sacred place, where seriousness and moderation reign, in the bosom of silence and religious retirement; there a minister of the sanctuary, surrounded by a chosen number of the faithful, utters from time to time some serious and solemn words. This is the personification of the Church in times disastrous from weakened faith and corrupted

morals. One of the rules of conduct of the Catholic Church has been, not to bend before the powerful. When she has proclaimed a law, she has proclaimed it for all, without distinction of rank. In the time of the power of those petty tyrants, who, under different names, persecuted the people, this conduct of the Church contributed in an extraordinary degree to render the ecclesiastical laws popular; for nothing was more likely to make a law tolerable to the people than to show that it applied to nobles, and even to kings. In the times of which we speak, hatred and violence among plebeians were severely proscribed; but the same law extended to great men and to royalty. A short time after the establishment of Christianity in England, we find a very curious example in that country, applicable to this question. It is nothing less than excommunication pronounced against three kings in the same year, and in the same town; all these were compelled by the Councils to do penance for the crimes which they had committed. The town of Llandaff, in Wales, within the metropolitan see of Canterbury, witnessed the celebration of three Councils, in the year 560. In the first, Monric, king of Glamorgan, was excommunicated for having put to death King Cinétha, although he had sworn the peace on the sacred relics; in the second, King Morcant was excommunicated for having put to death Friac, his uncle, in whose favor he had equally sworn the peace; in the third, King Guidnert was excommunicated for having put to death his brother, the competitor for the throne.

Thus, these barbarian chiefs, just changed into kings, and prone to slaughter, are compelled to acknowledge the authority of a superior power, and to expiate by penance the murder of their relatives and the violation of sacred engagements; it is useless to point out how much this must have contributed to the improvement of manners. "It was easy," the enemies of the Church will say—those who endeavor to lower the merit of her acts—"it was easy to preach gentleness of manners, to impose the observance of divine precepts on chiefs whose power was limited, and who had only the name of kings; it was easy to manage those petty barbarian chiefs, who, rendered fanatical by a religion of which they understood nothing,

humbly bowed before the first priest who ventured to menace them on the part of God. But of what importance was that? What influence could it have on the course of great events? The history of European civilization presents a vast theatre, where events must be studied on a large scale, and where none but the most important scenes exercised any influence on the spirit of nations." Let us observe, that these petty barbarian kings were the origin of the principal families which now occupy the most important thrones of the world. To place the germ of real civilization in their hearts, was to graft the tree which was one day to overshadow the earth. But without staying to show the futility of such reasoning, and as our opponents desire great scenes capable of influencing European manners on a large scale, let us open the history of the Church in the first ages, and we shall soon find a page which redounds to the eternal honor of Catholicity. The whole of the known world was subject to an emperor, whose name, then universally venerated, will continue to be respected by the remotest posterity. In an important city, the rebellious inhabitants put to death the commander of the garrison; the emperor, transported with anger, orders them to be exterminated. Returning to himself, he revokes the order; but it was too late, the order was executed, and thousands of victims had been involved in the horrible carnage; at the news of this dreadful catastrophe, a bishop quits the court of the emperor, leaves the city, and writes to him in this grave language: "I dare not offer the sacrifice if you attempt to be present at it; the blood of one innocent person would suffice to forbid me; how much more the massacre of a large number." The emperor, confident in his power, takes no notice of this letter, and goes towards the church. When he arrives at the door, he finds himself in the presence of a venerable man, who, with a grave and stern countenance, stops him and forbids him to enter the church. "Thou hast imitated David in crime," he says, "imitate him also in penance." The emperor yields, humbles himself, and submits to the regulations of the bishop, and religion and humanity gain an immortal triumph. This unhappy city was Thessalonica; the emperor was Theodosius; the prelate was St. Ambrose, Archbishop of Milan.

We find face to face, in this sublime fact, force and justice personified. Justice triumphs over force; but why? Because he who represents justice, represents it in the name of Heaven; because the sacred vestments and the imposing attitude of the man who stops the emperor reminds Theodosius of the divine mission of the holy bishop, and of the office which he holds in the sacred ministry. Put a philosopher in the place of the bishop, and tell him to arrest the proud culprit by an injunction of doing penance, and you will see whether human wisdom can do as much as the Catholic priest speaking in the name of God. Put, if you please, a bishop of the Church, who has acknowledged spiritual supremacy in the civil power, and you will see whether in his mouth words have the same effect in obtaining so glorious a triumph. The spirit of the Church was always the same; her arms were always directed towards the same end; her language was always equally strict, equally strong, whether she spoke to the Roman plebeian or a barbarian, whether she addressed her admonitions to a patrician of the empire or to a noble German. She was no more afraid of the purple of the Cæsars than of the frowns of the long-haired kings. The power which she possessed during the middle ages was not exclusively owing to her having preserved alone the light of science and the principles of government; but it was also owing to the invincible firmness, which no resistance and no attack could destroy. What would Protestantism have effected in such difficult and dangerous circumstances? Without authority, without a centre of action, without security for her own faith, without confidence in her resources, what means would she have had to assist her in restraining the torrent of violence—that impetuous torrent, which, after having inundated the world, was about to destroy the remains of ancient civilization, and opposed to all attempts at social reorganization an obstacle almost insurmountable? Catholicity, with its ardent faith, its powerful authority, its undivided unity, its well-compacted hierarchy, was able to undertake the lofty enterprise of improving manners; and it brought to the undertaking that constancy which is inspired by conscious strength, and that boldness which animates a mind secure of triumph.

We must not, however, imagine that the conduct of the Church, in her mission of improving manners, always brought her into collision with force. We also see her employ indirect means, limit her demands to what she could obtain, and ask for as little, in order to obtain as much as possible. In a capitulary of Charlemagne, given at Aix-la-Chapelle in 813, and consisting of twenty-six articles, which are nothing more than a sort of confirmation and *résumé* of the five Councils held a little before in France, we find in an appendix of two articles the method of proceeding judicially against those who, under pretext of the right called *faida*, excited tumults on Sundays, holidays, and also working days. We have already seen above that they had recourse to the holy relics, to give greater authority to the oaths of peace and friendship taken by kings towards each other—an august act, in which Heaven was invoked to prevent the effusion of blood, and to establish peace on earth. We see in the capitulary which we have just quoted, that the respect for Sundays and holidays was made use of to bring about the abolition of the barbarous custom, which authorized the relations of a murdered man to avenge his death in the blood of the murderer. The deplorable state of European society at that time is vividly painted by the means which the ecclesiastical power was compelled to use, to diminish in some degree the disasters occasioned by the prevailing violence. Not to attack, not to maltreat any one, not to have recourse to force to obtain reparation or to gratify a desire of vengeance, appears to us to be so just, so reasonable, and so natural, that we can hardly imagine another way of acting. If, now, a law were promulgated, to forbid one to attack one's enemy on such or such a day, at such or such an hour, it would appear to us the height of folly and extravagance. But it was not so at that time; such prohibitions were made continually, not in obscure hamlets, but in great towns, in very numerous assemblies, when bishops were present in hundreds, and where counts, dukes, princes, and kings were gathered together. This law, by which authority was glad to make the principles of justice respected, at least on certain days,—principally on the great solemnities,—this law, which now would appear to us so strange, was, in a certain way, and for a long period,

one of the chief points of public and private law in Europe. It will be understood that I allude to the truce of God, a privilege of peace very necessary at that time, as we see it very often renewed in various countries. Of all that I might say on this point, I shall content myself with selecting a few of the decisions of Councils at the time. The Council of Tubuza, in the diocese of Elne, in Roussillon, held by Guifred, Archbishop of Narbonne, in 1041, established the truce of God, from the evening of Friday until Monday morning. Nobody during that time could take any thing by force, or revenge any injury, or require any pledge in surety. Those who violated this decree were liable to the same legal composition as if they had merited death; in default of which, they were excommunicated and banished from the country.

The practice of this ecclesiastical regulation was considered so advantageous, that many other Councils were held in France during the same year, on the same subject. Moreover, care was taken frequently to repeat the obligation, as we see by the Council of Saint Gilles, in Languedoc, held in 1042, and by that of Narbonne, held in 1045. In spite of these, repeated efforts did not obtain all the desired fruit; this is indicated by the changes which we observe in the regulations of the law. Thus we see that, in the year 1047, the truce of God was fixed for a less time than in 1041; the Council of Telugis, in the same diocese of Elne, held in 1047, only ordains that it is forbidden to any one in all the *comté* of Roussillon to attack his enemy between the hours of none on Sunday and prime on Monday; the law was then much less extensive than in 1041, when, as we have seen, the truce of God was extended from Friday evening till Monday morning. We find in the same Council a remarkable regulation, the object of which was to preserve from all attack men who were going to church or returning from it, or who were accompanying women. In 1054, the truce of God had gained ground; we see it extended, not only from Friday evening till Monday morning after sunrise, but over considerable periods of the year. Thus we see that the Council of Narbonne, held by Archbishop Guifred, in 1045, after having included in the truce of God the time

from Friday evening till Monday morning, declares it obligatory during the following periods: from the first Sunday of Advent till the octave of the Epiphany; from Quinquagesima Sunday till the octave of Easter; from the Sunday preceding the Ascension till the octave of Pentecost; the festival days of Our Lady, of St. Peter, of St. Laurence, of St. Michael, of All Saints, of St. Martin, of St. Just and Pasteur, titularies of the Church of Narbonne, and all fasting days, under pain of anathema and perpetual banishment. The same Council gives some other regulations, so beautiful that we cannot pass them over in silence, when we are engaged in showing the influence of the Catholic Church in improving manners. The 9th canon forbids the cutting of olive-trees; a reason for it is given, which, in the eyes of jurists, will not appear sufficiently general or adequate, but which, in the eyes of the philosophy of history, is a beautiful symbol of the beneficial influence exercised over society by religion. This is the reason given by the Council: "It is," it says, "*that the olive-trees may furnish matter for the holy chrism, and feed the lamps that burn in the churches.*" Such a reason was sure to produce more effect than any that could be drawn from Ulpian and Justinian. It is ordained in the 10th canon that shepherds and their flocks shall enjoy at all times the security of the truce; the same favor is extended by the 11th canon to all houses within thirty paces of the churches. The 18th canon forbids those who have a suit, to take any active steps, to commit the least violence, until the cause has been judged in presence of the bishop and lord of the place. The other canons forbid the robbing of merchants and pilgrims, and the commission of wrong against any one, under pain of being separated from the Church, if the crime be committed during the time of the truce.

In proportion as we advance in the 11th century, we see the salutary practice of the truce of God more and more inculcated; the Popes interpose their authority in its favor. At the Council of Gironne, held by Cardinal Hugues-le-Blanc, in 1068, the truce of God is confirmed by the authority of Alexander II., under pain of excommunication; the Council held in 1080, at Lillebonne, in Normandy, gives us reason to suppose that the truce was then generally established, since it

ordains, by its first canon to bishops and lords, to take care that it was observed, and to inflict on offenders against it censures and other penalties. In the year 1093, the Council of Troja, in Apulia, held by Urban II., continues the truce of God. To judge of the extent of this canonical regulation, we should know that this Council consisted of sixty-five bishops. The number was much greater at the Council of Clermont, in Auvergne, held by the same Urban II., in 1095; it reckoned no less than thirteen archbishops, two hundred and twenty bishops, and a great number of abbots. The first canon of this Council confirms the truce for Thursday, Friday, Saturday, and Sunday; it wishes, moreover, that it should be observed on all the days of the week, with respect to monks, clergy, and women. The canons 29 and 30 ordain, that if a man pursued by an enemy take refuge near a cross, he should be in safety, as if he had found asylum in a church. The sublime sign of redemption, after having given salvation to the world, by drinking on Calvary the blood of the Son of God, had already proved a refuge, during the sack of Rome, to those who fled from the fury of the barbarians; centuries later, we find it erected on the roads, to save the unfortunate, who, by embracing it, escaped their enemies, who were thus deterred from vengeance.

The Council of Rouen, held in 1096, extending still further the benefit of the truce, ordains the observance of it from the Sunday before Ash Wednesday till the second feast after the octave of Pentecost, from sunset on Wednesday preceding Advent to the octave of Epiphany, and every week from Friday after sunset till the Monday following at sunrise; in fine, on all the feasts and vigils of the Virgin and the Apostles. The 2d canon of the same Council secures perpetual peace to all clergy, monks, and nuns, to women, to pilgrims, to merchants and their servants, to oxen and horses of labor, to carmen and laborers; it gives the same privileges to all lands that belong to sacred institutions; all such persons, animals, and lands are protected from the attacks of pillage and all kinds of violence. At this time the law felt itself stronger; it could now call for obedience in a firmer tone; we see, indeed, that the third canon of

the same Council enjoins upon all who have reached the age of twelve, to engage by oath to observe the truce; in the fourth canon, all who refuse to take this oath are excommunicated. Some years after, in 1115, the truce, instead of comprising certain stated parts of the year, embraces whole years; the Council of Troja in Apulia, held in that year by Pope Pascal, establishes the truce for three years.

The Popes pursued with ardor the work thus commenced; they sanctioned it with their authority, and extended the observance of the truce by means of their influence, then universal and powerful over all Europe. Although the truce was apparently only a testimony of respect paid to religion by the violent passions, which, in her favor, consented to suspend their hostilities, it was, in reality, a triumph of right over might, and one of the most admirable devices ever used to improve the manners of a barbarous people. The man who, during four days of the week, and during long periods of the year, was compelled to suspend the exercise of force, was necessarily led to more gentle manners; he must, in the end, entirely renounce it. The difficulty is not, to convince a man that he does ill, but to make him lose the habit of doing so; and it is well known that habits are engendered by the repetition of acts, and are lost when they cease for a time. Nothing is more pleasing to the Christian soul than to see the Popes laboring to maintain and extend this truce. They renew the command of it with a power the more efficacious and universal according to the number of bishops who assist at the Councils where their supreme authority presides. At the Council of Rheims, opened by Pope Calixtus II. in person, in 1119, a decree confirming the truce is promulgated. Thirteen archbishops, more than two hundred bishops, and a great number of abbots and ecclesiastics, distinguished for their rank, assisted at this Council. The same command is renewed at the General Council of Lateran, held under the care of the same Pontiff, Calixtus II., in 1123. There were assembled more than three hundred archbishops and bishops, and more than six hundred abbots. In 1130, the Council of Clermont, in Auvergne, held by Innocent II., insists on the same point, and repeats the regulations concerning the observance of the

truce. The Council of Avignon, held in 1209, by Hugh, Bishop of Riez, and Milon, notary of Pope Innocent III., both legates of the Holy See, confirms the laws before enacted on the subject of the peace and the truce, and condemns the rebellious who dare to infringe them. In the year 1215, at the Council of Montpellier, assembled by Robert de Courçon, and presided over by Cardinal Benavent, in his office as legate of the province, all the regulations established at different times for the public safety, and more recently to secure peace between lord and lord, and town and town, are renewed and confirmed.

Those who have regarded the intervention of the ecclesiastical power in civil affairs as a usurpation of the rights of public authority, should tell us how it is possible to usurp that which does not exist, and how a power which is unable to exercise the authority which ought to belong to it, can reasonably complain when that authority passes into the hands of those who have force and skill to make use of it. At that time, the public authority did not at all complain of these pretended usurpations. Governments and nations looked upon them as just and legitimate; for, as we have said above, they were natural and necessary, they were brought about by the force of events, they were the result of the situation of affairs. Certainly, it would now seem extraordinary to see bishops provide for the security of roads, publish edicts against incendiaries, against robbers, against those who cut down olive-trees and commit other injuries of the kind; but, at the time we are speaking of, this proceeding was very natural, and more, it was necessary. Thanks to the care of the Church, to that incessant solicitude which has been since so inconsiderately blamed, the foundations of the social edifice, in which we now dwell in peace, were laid; an organization was realized which would have been impossible without the influence of religion and the action of ecclesiastical authority. If you wish to know whether any fact of which you have to judge is the result of the nature of things, or the fruit of well contrived combinations, observe the manner in which it appears, the places where it takes its rise, the times which witness its appearance; and if

you shall find it reproduced at once in places far distant from each other, by men who can have had no concert, be assured that it is not the result of human contrivance, but of the force of events. These conditions are found united in a palpable manner in the action of the ecclesiastical power on public affairs. Open the Councils of those times, and everywhere the same facts meet your eyes; thus, to quote a few examples, the Council of Palencia, in the kingdom of Leon, held in 1129, decrees, in its 12th canon, exile or seclusion in a monastery, against those who attack the clergy, monks, merchants, pilgrims, and women. Let us pass into France; the Council of Clermont, in Auvergne, held in 1130, pronounces, in its 13th canon, excommunication against incendiaries. In 1157, the Council of Rheims, in the 3d canon, orders to be respected, during war, the persons of the clergy, of monks, women, travellers, laborers, and vine-dressers. Let us pass into Italy; the 11th Council of Lateran, a General Council, convoked in 1179, forbids, in its 22d canon, to maltreat or disturb monks, clergy, pilgrims, merchants, peasants, either travelling or engaged in the labors of agriculture, and animals laboring in the fields. In its 24th canon, the same Council excommunicates those who make slaves of, or rob, Christians on voyages of commerce, or for other lawful purposes; those who plunder the shipwrecked are subjected to the same penalty, unless they make restitution. Let us go to England; there the Council of Oxford, held in 1222, by Stephen Langton, Archbishop of Canterbury, forbids, by its 20th canon, any one to have robbers in their service. In Sweden, the Council of Arbogen, held in 1396, by Henry, Archbishop of Upsala, directs, by its 5th canon, that church-burial shall be refused to pirates, ravishers, incendiaries, highway robbers, oppressors of the poor, and other malefactors; so that in all parts, and at the same periods, we see the same fact appear, viz. the Church struggling against injustice and violence, and endeavoring to substitute in their stead the empire of law and justice.

In what spirit must they read the history of the Church, who do not feel the beauty of the picture presented to us by the multitude of

regulations, scarcely indicated here, all tending to protect the weak against the strong? The clergy and monks, on account of the weakness consequent on their peaceful profession, find in the canons which we have just quoted peculiar protection; but the same is granted to females, to pilgrims, to merchants, to villagers, travelling, or engaged in rural labors, and to beasts of labor—in a word, to all that is weak; and observe, that this protection is not a mere passing effort of generosity, but a system practised in widely different places, continued for centuries, developed and applied by all the means that charity suggests—a system inexhaustible in resources and contrivances, both in producing good and in preventing evil. And surely it cannot be said that the Church was influenced in this by views of self-interest: what interested motive could she have in preventing the spoliation of an obscure traveller, the violence inflicted on a poor laborer, or the insult offered to a defenceless woman? The spirit which then animated her, whatever might be the abuses which were introduced during unhappy times, was, as it now is, the spirit of God himself—that spirit which continually communicates to her so marked an inclination towards goodness and justice, and always urges her to realize, by any possible means, her sublime desires. I leave the reader to judge whether or not the constant efforts of the Church to banish the dominion of force from the bosom of society were likely to improve manners. I now speak only of times of peace; for I need not stay to prove that during the time of war that influence must have had the happiest results. The *væ victis* of the ancients has disappeared from modern history, thanks to the divine religion which knew how to inspire man with new ideas and new feelings—thanks to the Catholic Church, whose zeal for the redemption of captives has softened the fierce maxims of the Romans, who, as we have seen, had considered it necessary to take from brave men the hope of being redeemed from servitude, when by the chances of war they had fallen into the hands of their enemies. The reader may revert to the seventh chapter of this work, and the third paragraph of the fifteenth note, where there are, in the original text, numerous documents that may be quoted in support of our assertion; he will thus be better able to

judge of the gratitude which is due to the charity, disinterestedness, and indefatigable zeal of the Catholic Church in favor of the unfortunate, who groaned in bondage in the power of their enemies. We must also consider that, slavery once abolished, the system was necessarily improved; for if those who surrendered could no longer be put to death, or be kept in slavery, the only thing to be done was, to retain them for the time necessary to prevent their doing mischief, or until they were ransomed. Now, this is the modern system, which consists in retaining prisoners till the end of the war, or until they are exchanged.

Although the amelioration of manners, as I have said above, consists, properly speaking, in the exclusion of force, we must yet avoid considering this exclusion of force in the abstract, and believing that such an order of things was possible, by virtue of the mere development of mind. All is connected in this world; it is not enough, to constitute the real improvement of manners, that they avoid violence as much as possible; they must also be benevolent. As long as they are not so, they will be less gentle than enervated; the use of force will not be banished from society, but it will remain artificially disguised. It will be understood, then, that we are obliged here to take a survey of the principle whence European civilization has drawn the spirit of benevolence which distinguishes it; we shall thus succeed in showing that the gentleness of our present manners is principally owing to Catholicity. There is, besides, in the examination of the principle of benevolence, so much importance of its own, independently of its connection with the question which now occupies us, that we cannot avoid devoting some pages to it, in the course of an analytical review of the elements of our civilization.²²

CHAPTER XXXIII.

ON THE DEVELOPMENT OF PUBLIC BENEFICENCE IN EUROPE.

Never will manners be perfectly gentle without the existence of public beneficence; so that gentleness of manners and beneficence, although distinct, are sisters. Public beneficence, properly so called, was unknown among the ancients. Individuals might be beneficent there, but society was without compassion. Thus, the foundation of public establishments of beneficence formed no part of the system of administration among ancient nations. What, then, did they do with the unfortunate? We will answer with the author of the *Génie de Christianisme*, that they had no resources but infanticide and slavery. Christianity having become predominant everywhere, we see the authority of the Church employed in destroying the remains of cruel customs. In the year 442, the Council of Vaison, establishing a regulation for the legitimate possession of foundlings, decrees ecclesiastical censure against those who disturb by importunate reproaches charitable persons who have received children. The Council adopts this measure with the view of protecting a beneficent custom; for, adds the canon, *these children were exposed to be eaten by dogs*. There were still found fathers unnatural enough to kill their children. The Council of Lerida, held in 546, imposes seven years of penance on those who commit such a crime; and that of Toledo, held in 589, forbids, in the 17th canon, parents to commit this crime. Still, the difficulty did not consist in correcting these excesses; crimes thus opposed to the first notions of morality—so much in contradiction to the feelings of nature—tended to their own extirpation. The difficulty consisted in finding proper means to organize a vast system of beneficence, to provide constant succor,

not only for children, but for old men, for the sick, for the poor incapable of living by their own labor; in a word, for all the necessitous. Familiarized as we are with such a system universally established, we see nothing in it but what is simple and natural; we can hardly find any merit in it. But let us suppose for a moment that such institutions do not exist; let us transport ourselves to the times when there was not even the first idea of them, what continued efforts would there not be required to establish and organize them!

It is clear that by the mere extension of Christian charity in the world the various wants of humanity must have been more frequently succored, and with more efficacy, than they were before; and this even if we suppose that the exercise of charity was limited to purely individual means. Assuredly, there would always have been a great number of the faithful who would have remembered the doctrines and example of Jesus Christ. Our Saviour did not content Himself with teaching us by his discourses the obligation of loving our neighbor as ourselves, nor with a barren affection, but by giving food to the hungry, drink to the thirsty, clothes to the naked; by visiting the sick and prisoners. He showed us in his own conduct a model of the practice of charity. He could have shown in a thousand ways the power which belonged to Him in heaven and on earth; his voice could have controlled all the elements, stopped the motions of the stars, and suspended all the laws of nature; but He delighted above all in displaying his beneficence; He only attested his divinity by miracles which healed or consoled the unfortunate. His whole life is summed up in the sublime simplicity of these two words of the sacred text: *pertransiit benefaciendo; He went about doing good.*

Whatever good might be expected from Christian charity when left to its own inspiration, and acting in a sphere purely individual, it was not desirable to leave it in this state. It was necessary to realize it in permanent institutions, and not to leave the consolation of the unfortunate to the mercy of man and passing circumstances; this is the reason why there was so much wisdom and foresight in the idea of founding establishments of beneficence. It was the Church that

conceived and executed this idea. Therein she only applied to a particular case her general rule of conduct; which is, never to leave to the will of individuals what can be connected with an institution: and observe, that this is one of the causes of the strength inherent in all that belongs to Catholicity. As the principle of authority in matters of faith preserves to her unity and constancy therein, so the rule of intrusting every thing to institutions secures the solidity and duration of all her works. These two principles have an intimate connection; for if you examine them attentively, the one supposes that she distrusts the intellect of man, the other, that she distrusts his individual will and capacity. The one supposes that man is not sufficient of himself to attain to, and preserve the knowledge of, certain truths; the other, that he is so feeble and capricious, that it is unwise to leave to his weakness and inconstancy the care of doing good. Now, neither one nor the other is injurious to man; neither one nor the other lowers his proper dignity. The Church only tells him, that he is, in reality, subject to error, inclined to evil, inconstant in his designs, and very miserable in his resources. These are melancholy truths; but the experience of every day attests them, and the Christian religion explains them, by establishing, as a fundamental dogma, the fall of man in the person of our first parent. Protestantism, following principles diametrically opposite, applies the same spirit of individuality to the will as to the intelligence; it is even the natural enemy of institutions. Without going further than our present subject, we see that its first step, on its appearance, was to destroy what existed, without in any way replacing it. Will it be believed that Montesquieu went so far as to applaud this work of destruction? This is another proof of the fatal influence exerted over minds by the pestilential atmosphere of the last century: "Henri VIII.," says Montesquieu, "voulant réformer l'église d'Angleterre, détruisit les moines: nation paresseuse elle-même, et qui entretenait la paresse des autres, parceque, pratiquant l'hospitalité, une infinité de gens oisifs, gentilhommes et bourgeois, passoient leur vie à courir de couvent en couvent. *Il ôta encore les hôpitaux, où le bas peuple trouvait sa subsistance*, comme les gentilhommes trouvaient la leur dans les monastères. Depuis ce changement, l'esprit de

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